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In re Patent Application of

TAMURA

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Filed: January 19, 2001

Examiner: Ferguson

For: HEAT-RESISTANT GLASS FIBER AND PROCESS FOR THE PRODUCTION THEREOF

\* \* \* \* \*

Assistant Commissioner for Patents

Washington, DC 20231

Sir:

**DECLARATION**

I, Shinichi TAMURA of c/o NITTO BOSEKI CO., LTD., 1, Aza Higashi, Gonome, Fukushima-shi, Fukushima-ken Japan declare that:

1. I graduated from Kyoto Institute of Technology, Faculty of Engineering and Design, Department of Chemistry and Materials Technology in March 1983. I have been employed by NITTO BOSEKI CO., LTD., one of assignees of the above identified application, where I have been engaged in research and development of glass fibers.
2. I am the sole inventor of the above identified application and am familiar with the subject matter disclosed in said application.
3. I am familiar with the Official Actions of April 24 and November 4, 2002 and the documents cited therein.

4. I acknowledge that Eastes et al. US patent 5,789,329 cited by the Examiner discloses a glass fiber consisting essentially of 59.0 to 62.0 wt% of  $\text{SiO}_2$ , 20.0 to 24.0 wt% of  $\text{CaO}$ , 12.0 to 15.0 wt% of  $\text{Al}_2\text{O}_3$ , 1.0 to 4.0 wt% of  $\text{MgO}$ , 0.0 to 0.5 wt% of  $\text{F}_2$ , 0.1 to 2.0 wt% of  $\text{Na}_2\text{O}$ , 0.0 to 0.9 wt% of  $\text{TiO}_2$ , 0.0 to 0.5 wt% of  $\text{Fe}_2\text{O}_3$ , 0.0 to 2.0 wt% of  $\text{K}_2\text{O}$  and 0.0 to 0.5 wt% of  $\text{SO}_3$ , and the lower limit of  $\text{SiO}_2$  is 59.0 %, which is slightly higher than the upper limit of  $\text{SiO}_2$  content of 58.5 % in the present invention.

5. Prior to the completion of the present invention, I was familiar with the above mentioned US patent 5,789,329. Therefore, I have conducted follow-up experiment with respect to the invention disclosed in the above mentioned US patent 5,789,329 and disclosed the results of the follow-up experiment in the present specification. The following experiments were conducted by me or under my supervision and control and to the best of my information the data herein are correct and accurate.

As explained on page 10, lines 27-28 of the present application, Comparative Example 3 corresponds to an Example of the above mentioned US patent 5,789,329, the experimental results of which are shown in Table 2 of the present specification.

I confirm below the text of Examples and Comparative Examples, that is, procedures in Examples 1-5 which are typical examples of the present invention and Comparative Example 3 which is a typical example of the above mentioned US patent 5,789,329 as well as experimental results obtained in Examples 1-5 and Comparative Example 3.

Examples 1 – 5 and Comparative Example 3

Raw materials for glasses were formulated to obtain compositions shown in Tables 1 and 2, and in each Example, the formulated raw materials were melted in a platinum crucible at 1,500°C for 8 hours. Then, molten glasses were cast on carbon plates to obtain glass samples. Tables 1 and 2 show spinning temperatures, liquidus temperatures,  $\Delta T$  and softening points of the glass samples, which were measured with the methods described on pages 8 and 9 of the present specification.

Then, glass fibers having an average diameter of 13  $\mu\text{m}$  were spun from the above glass samples according to a conventional method. Tables 1 and 2 show acid treatment properties of the glass fibers, which were measured with the methods disclosed on page 9 of the present specification.

Then, the above glass fibers were immersed in a 3 wt% solution of hydrochloric acid at 70°C for 45 minutes, and the thus-treated glass fibers were washed with water and dried to obtain acid-treated glass fibers. Tables 1 and 2 report heat resistance of each of these acid-treated glass fibers and thickness of the surface layer portion of each acid-treated glass fiber which surface layer portion had an  $\text{SiO}_2$  content of at least 90 % by weight.

**Table 1**

		Example				
		1	2	3	4	5
Glass Composition (wt%)	SiO <sub>2</sub>	58.0	57.7	57.5	58.0	57.7
	B <sub>2</sub> O <sub>3</sub>	-	-	-	-	-
	Al <sub>2</sub> O <sub>3</sub>	16.0	13.5	14.3	13.0	15.0
	CaO	16.7	25.3	25.2	25.4	24.0
	MgO	8.3	3.0	2.8	3.0	2.8
	Na <sub>2</sub> O	0.0	0.0	0.0	0.0	0.0
	K <sub>2</sub> O	1.0	0.5	0.5	0.6	0.5
	Fe <sub>2</sub> O <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
	TiO <sub>2</sub>	-	-	-	-	-
	ZnO	-	-	-	-	-
Glass Properties	Spinning temperature(°C)	1,227	1,246	1,242	1,246	1,262
	Liquidus temperature(°C)	1,170	1,174	1,181	1,188	1,200
	ΔT (°C)	57	72	61	58	62
	Softening point (°C)	915	887	885	890	902
Properties of glass fibers	Acid treatment properties <sup>1)</sup> (%)	6.0	7.0	9.0	6.0	7.0
	Loss ratio after heating (%)	12	14	18	12	14
	Thickness of surface layer portion <sup>2)</sup> (μm)	0.64	0.75	0.98	0.60	0.70
	Heat resistance (900°C, 10 hours)	AA <sup>3)</sup>	AA	AA	AA	AA

(Notes)

1) Acid treatment properties: shown by a weight loss ratio based on acid treatment.

2) Thickness of surface layer portion: thickness of a surface layer portion having an SiO<sub>2</sub> content of at least 90 % by weight.

3) AA: A fiber nearly retains its flexibility.

Table 2

		Comparative Example
		3
Glass Compo- sition (wt %)	SiO <sub>2</sub>	60.0
	B <sub>2</sub> O <sub>3</sub>	-
	Al <sub>2</sub> O <sub>3</sub>	12.9
	CaO	23.1
	MgO	3.0
	Na <sub>2</sub> O	0.0
	K <sub>2</sub> O	0.6
	Fe <sub>2</sub> O <sub>3</sub>	0.3
	TiO <sub>2</sub>	0.1
	ZnO	-
Glass Prop- erties	Spinning temperature (°C)	1,278
	Liquidus temperature (°C)	1,192
	ΔT (°C)	86
	Softening point (°C)	916
Prop- erties of glass fibers	Acid treatment properties <sup>1)</sup> (%)	0.4
	Loss ratio after heating (%)	0.8
	Thickness of surface layer portion <sup>2)</sup> (μm)	0.04
	Heat resistance (900°C, 10 hours)	C <sup>3)</sup>

(Notes)

1) Acid treatment properties: shown by a weight loss ratio based on acid treatment.

2) Thickness of surface layer portion: thickness of a surface layer portion having an SiO<sub>2</sub> content of at least 90 % by weight.

3) C: Fibers are fused and deformed.

Based upon my thirty year experience with glass fibers generally and heat resistant glass fibers in particular and considering the data in Tables 1 and 2, I have

concluded in all of Examples 1 to 5 (according to the present invention) the  $\Delta T$  is at least 50°C so that the glasses are excellent in spinnability, and further, the glass fibers are excellent in acid treatment properties and have 0.60 to 0.98  $\mu\text{m}$  thick surface layer portions made of silicic glass (having an  $\text{SiO}_2$  content of at least 90 % by weight), so that they have excellent heat resistance.

In Comparative Example 3, the glass has a high  $\text{SiO}_2$  content and is excellent in spinnability. However, the glass fiber is poor in acid treatment properties, and since the surface layer portion made of a silicic glass has a thickness of only 0.04  $\mu\text{m}$ , the glass fiber is very poor in heat resistance.

In my opinion, these results clearly demonstrate the technical significance or criticality in the numerical restriction of the upper limit of  $\text{SiO}_2$  to 58.5 wt% in the present invention.

6. For further confirmation of the technical significance of numerical limitation of the upper limit of  $\text{SiO}_2$  to 58.5 wt%, I carried out a series of Experiments Nos. 1 to 6 in which the content of  $\text{SiO}_2$  was changed to 56, 57, 58, 58.5, 59 and 60 wt%, the content of  $\text{CaO}$  whose content was the second largest was changed to 26, 25, 24, 23.5, 23 and 22 wt% and the contents of the other components  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  were kept unchanged. Table 3 shows glass compositions. These glass compositions were melted under heat, and glass fibers were spun therefrom, in the same manner as in the method described in sections [0025] - [0026] of the present specification.

Each of the glass fibers obtained in Experiments Nos. 1 to 6 was immersed in 3 % hydrochloric acid at 70°C for 45 minutes, washed with water and dried in the same manner as in the method described in section [0026] of the present specification, to give acid-treated glass fibers. Table 3 shows weight loss ratios of the acid-treated glass fibers.

Table 3

Experiment No.	1	2	3	4	5	6
SiO <sub>2</sub>	56	57	58	58.5	59	60
Al <sub>2</sub> O <sub>3</sub>	15	15	15	15	15	15
CaO	26	25	24	23.5	23	22
MgO	2.5	2.5	2.5	2.5	2.5	2.5
Na <sub>2</sub> O	0	0	0	0	0	0
K <sub>2</sub> O	0.5	0.5	0.5	0.5	0.5	0.5
Total (wt%)	100	100	100	100	100	100
Weight loss ratio (%) HCl 3%, 70°C, 45 minutes	12.0	8.00	3.00	1.70	0.30	0.10


As shown in Table 3, when the SiO<sub>2</sub> content is 56 wt%, the weight loss ratio after the acid treatment is 12 wt%, and the glass fiber has remarkably excellent acid treatment properties. When the SiO<sub>2</sub> content is increased to 57 wt%, 58 wt% and 58.5 wt%, the weight loss ratio decreases but is 8.00 wt %, 3.00 wt% or 1.70 wt %. The glass fibers therefore have excellent acid treatment properties.

However, when the content of SiO<sub>2</sub> exceeds 58.5 wt% and reaches 59 wt%, the weight loss ratio comes to be smaller than 1 wt% and is 0.30 wt%, which value corresponds to 17.6 % of the weight loss ratio (1.70 wt%) obtained when the content of SiO<sub>2</sub> is 58.5 %. Further, the weight loss ratio when the content of SiO<sub>2</sub> is 60 % corresponds to 5 % of the weight loss ratio when the content of SiO<sub>2</sub> is 58.5 wt%. These results show that the SiO<sub>2</sub> content of 58.5 wt% has technical significance.

The undersigned declares that all statements made herein of his knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment's, or both, under section 1001 of Title 18 of the United States Code and such willful false

statements may jeopardize the validity of the application or any patent issuing thereon.

Dated this 19<sup>th</sup> day of March 2003

  
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Shinichi TAMURA